Perchlorate

An Integrated Approach to Reliable Perchlorate Analyses

May 12, 2004

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Agenda

- Perchlorate Chemistry and Sources
- Current Methods for Testing
- Ion Chromatography
- LC/MS/MS
- An Integrated Approach
- A Success Story
- Summary and Conclusions

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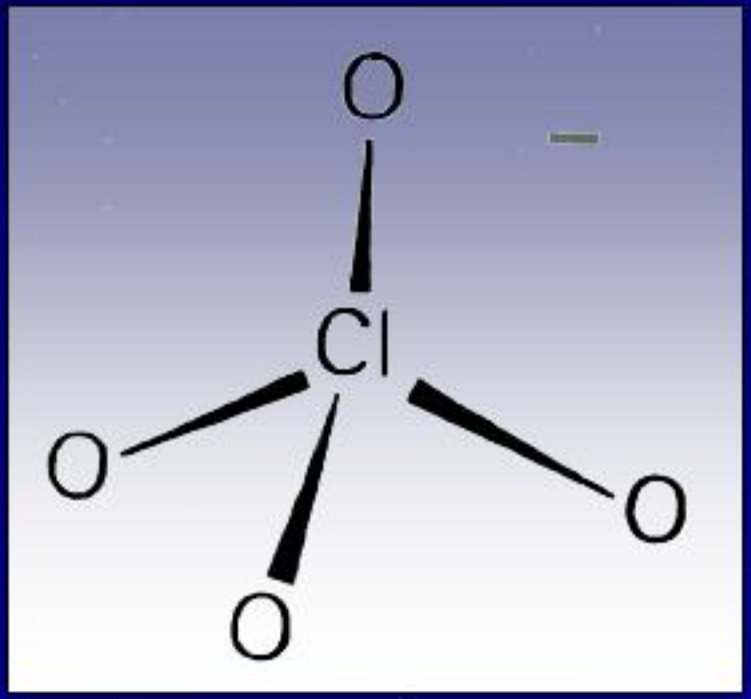
Perchlorate Ion



- Perchlorate is a compound containing one chlorine atom and four oxygen atoms.
- Perchlorate is an ion, meaning it carries an electrical charge, as indicated by the negative sign.

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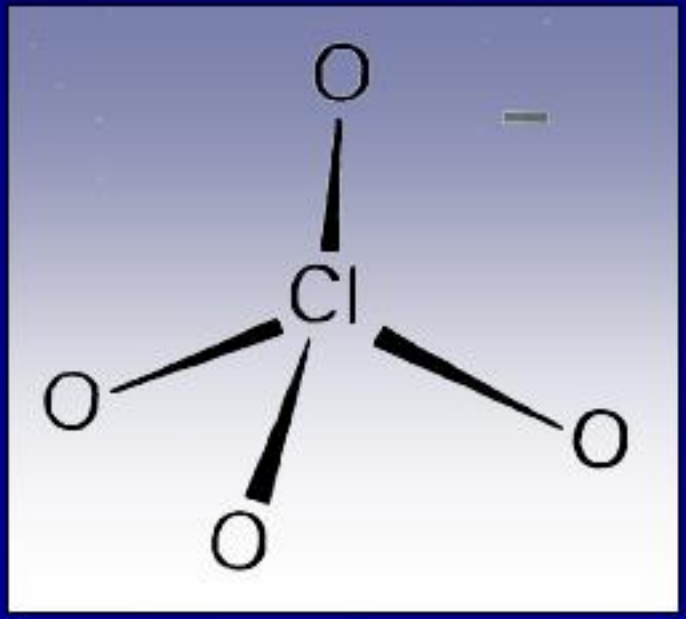
Natural Sources

- Chilean fertilizer deposits
- New Mexican potash
- Canadian potash
- Californian hanksite
- Bolivian playa crusts



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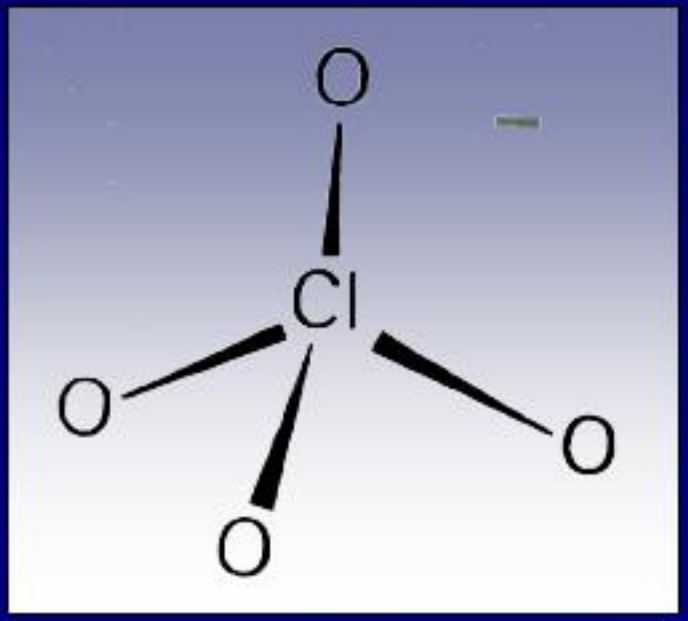
Anthropogenic Sources



- Rocket fuel
- Fireworks
- High explosives
- Flares
- Herbicides
- Automobile airbags
- Tracer munitions
- Detergents ?

How is Perchlorate Measured?

- Other analytical methods that can detect perchlorate:
  - IC - 2nd column confirmation & pre-concentration "Improved" Method 314.1
  - IC/MS - IC with mass spectrometer detection Proposed Method 330.0
  - LC/MS - liquid chromatography with MS detection
  - LC/MS/MS - Method 8321 Modified Proposed Method 331.0

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How is Perchlorate Measured?

- EPA Method 314.0
  - Ion chromatography (IC) with a conductivity detector
- Enhanced (Modified) 314.0
  - IC with a suppressed conductivity detection
- SW-846 Method 9058 (draft)
  - IC with a conductivity detector

Ion Chromatography

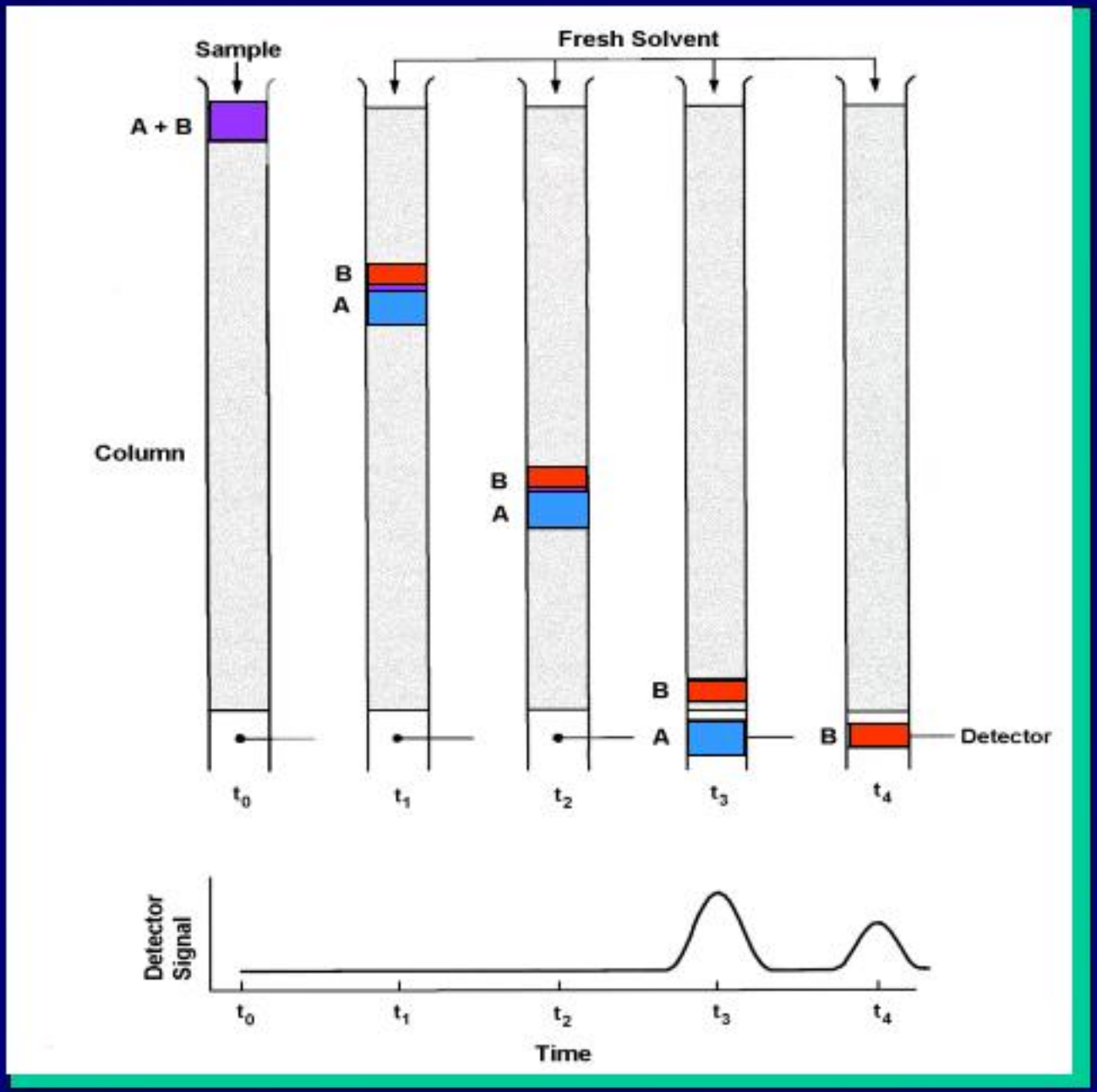

Diagram from *Fundamentals of Analytical Chemistry*, Skoog, 1988.

Identification of Perchlorate by IC

11.2.4 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards measured over several days. Three times the standard deviation of retention time may be used as a suggested window size but the retention time window should not extend beyond ± 5% of the retention time for perchlorate. The experience of the analyst should weigh heavily in the interpretation of these chromatograms.

EPA Method 314.0

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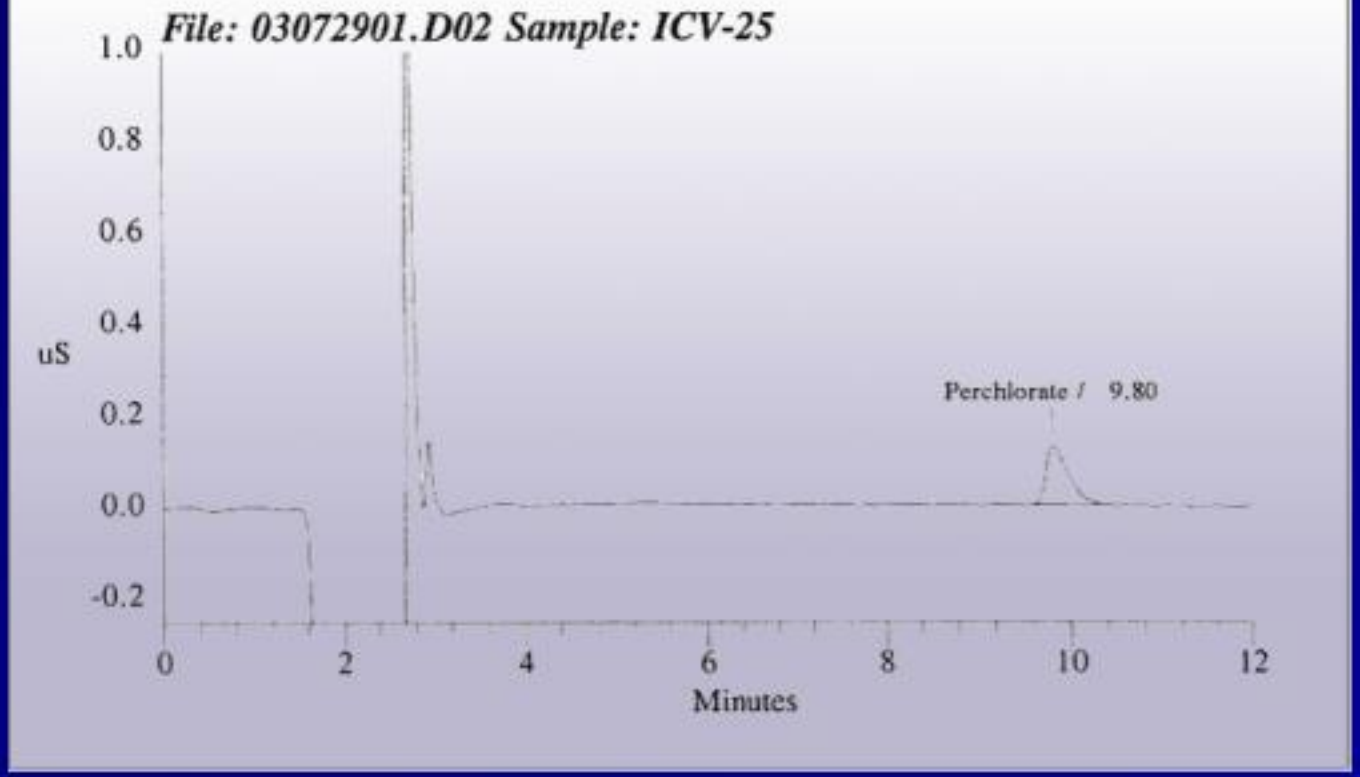
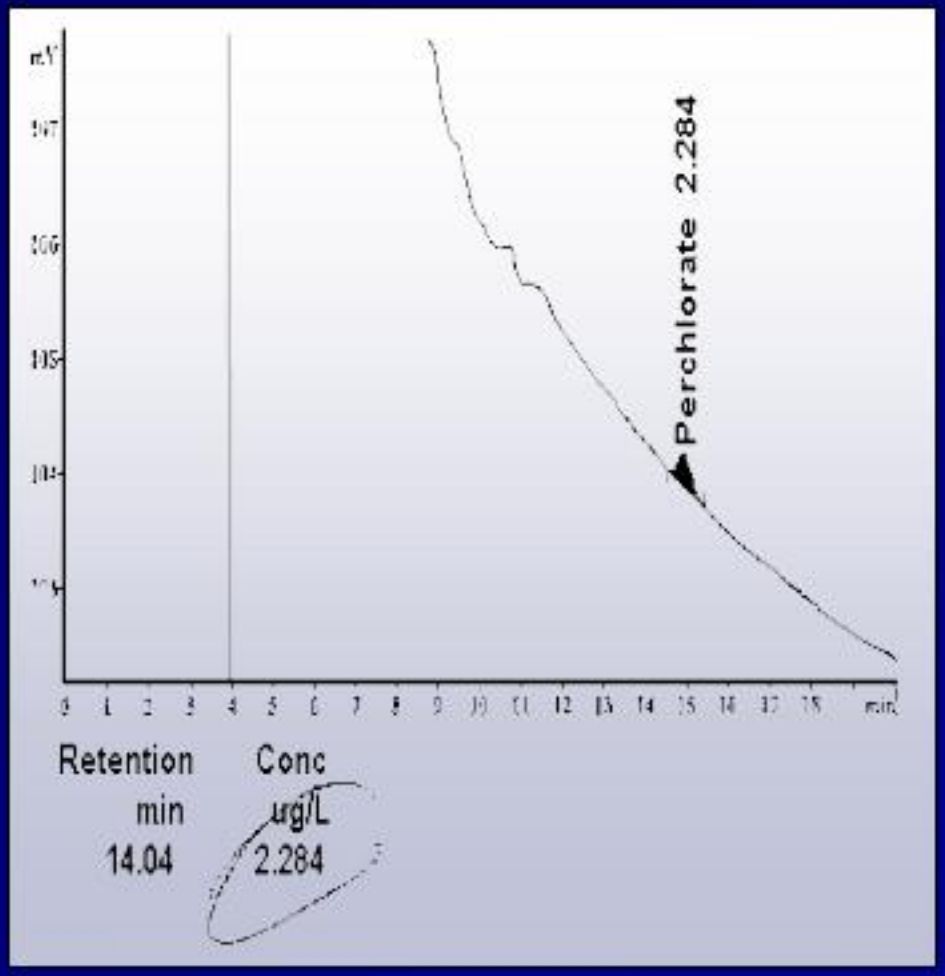
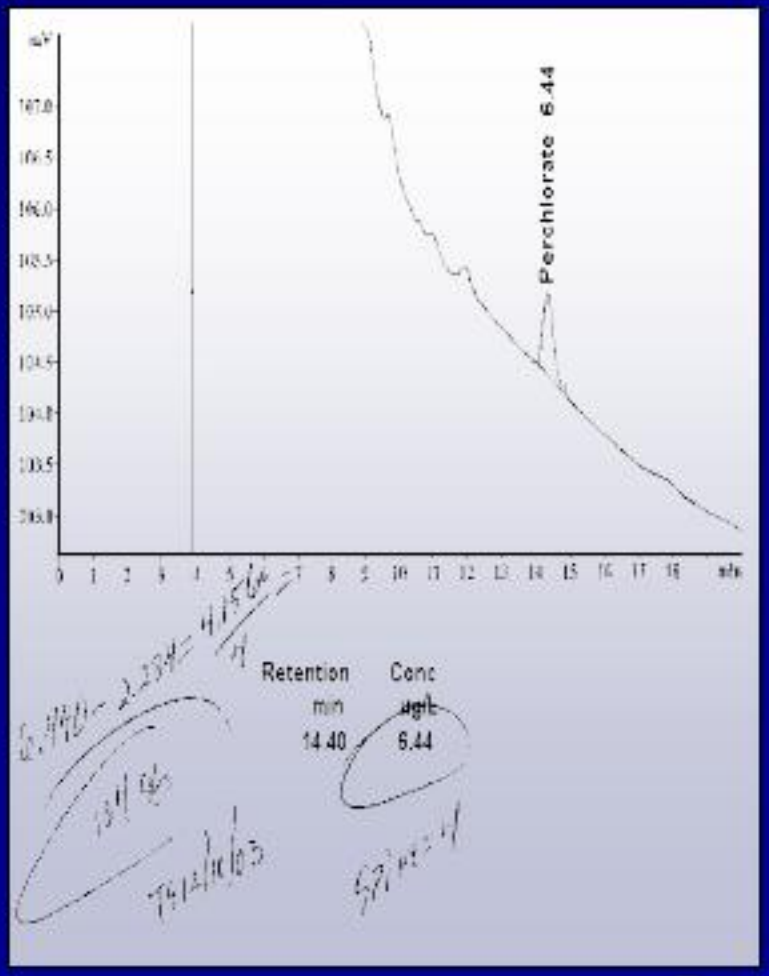
IC Perchlorate Standard

Ret Time	Component Name	Concentration UG/L	Height	Area
9.80	Perchlorate	23.777	127978	2164871
	Totals	23.777	127978	2164871



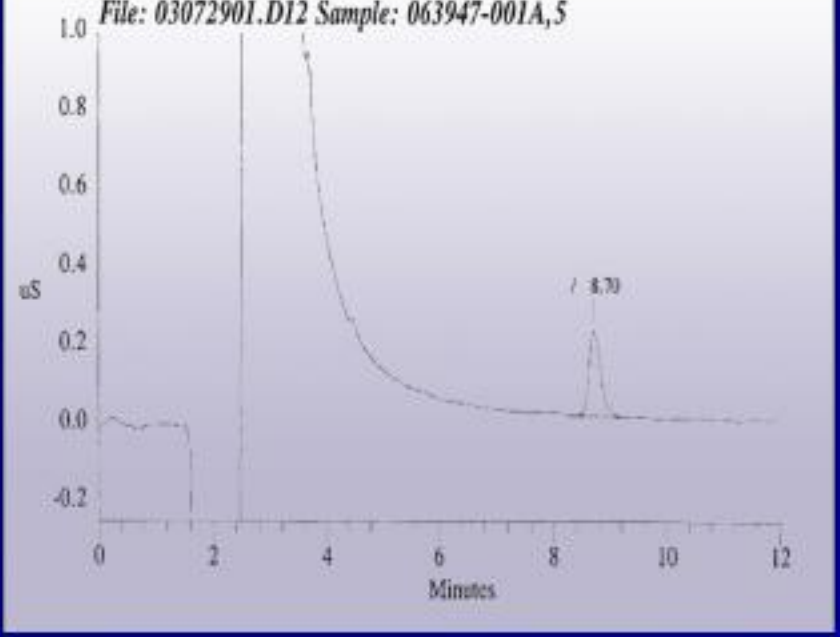
Matrix Spike Confirmation



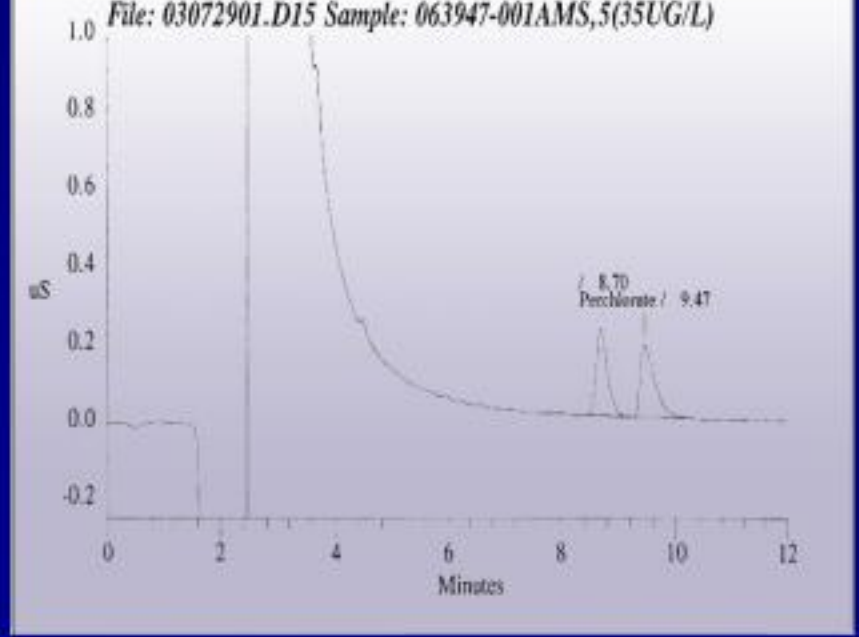


Matrix Spike Non-Confirmation

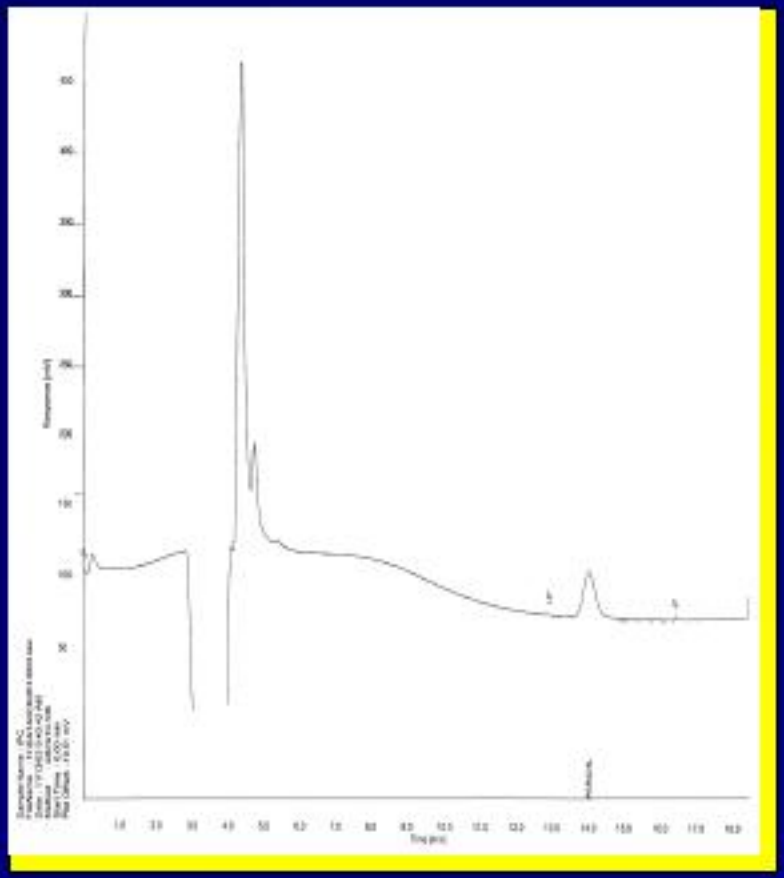
Ret Time	Component Name	Concentration UG/L	Height	Area
0.00	Perchlorate	0.000	0	0
	Totals	0.000	0	0

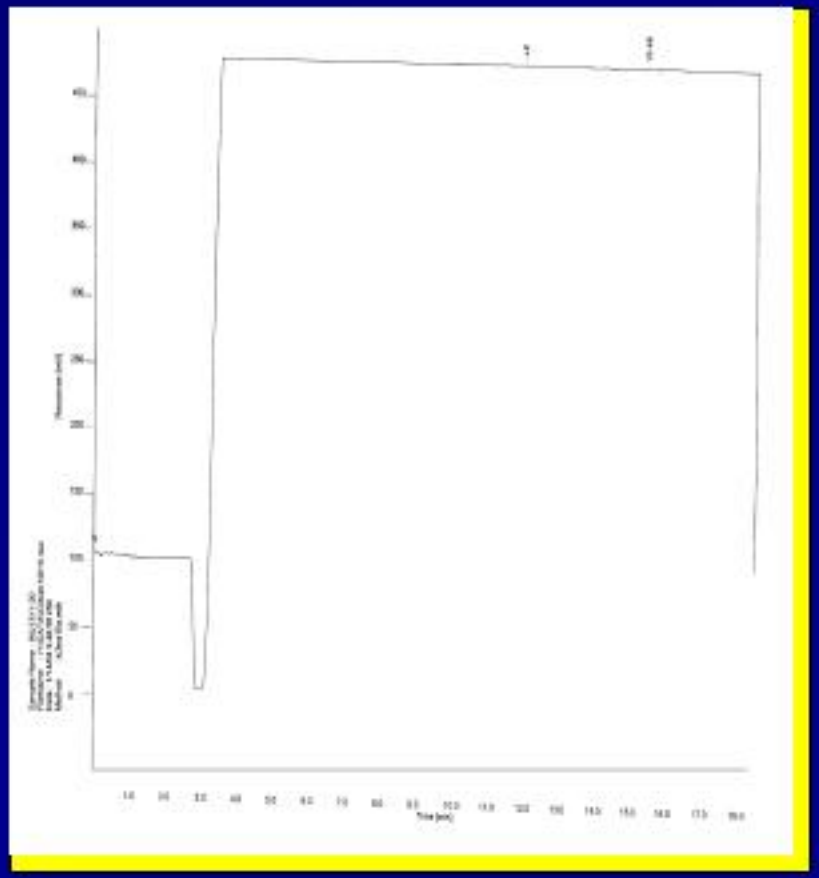


Ret Time	Component Name	Concentration UG/L	Height	Area
9.47	Perchlorate	35.128	183878	3225568
	Totals	35.128	183878	3225568



High Conductivity





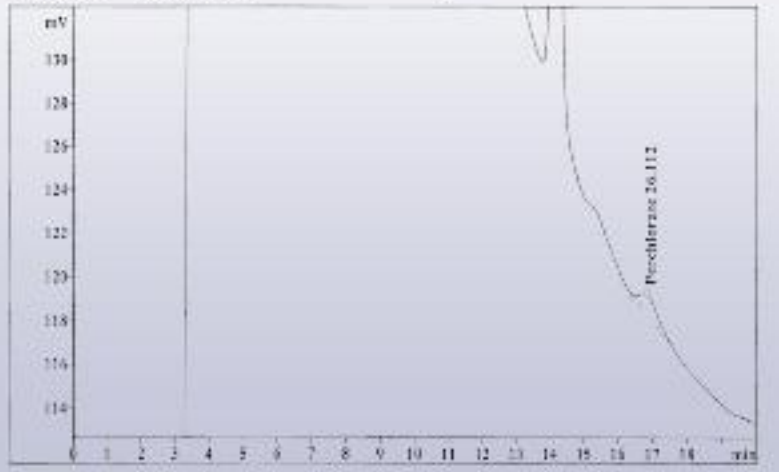
Carry-Over

SAMPLE:

Vial number: 21
Volume: 1.0 µl
Dilution: 2.00
Amount: 1.0000

COLUMN: DX-AS16
Size: 4.0 x 250 mm
Number: 02362
Part size: 5.0 µm
ELUENT: 35 NaOH
Flow: 1.10 mL/min
Temperature: 35.0°C
Pressure: 2430.0 psi

Conc was 14.56 µg/L
Needed 2x Dilution



Quantitation method: Custom

No	Retention min	Height mV	Area mV*sec	Conc. µg/L	Name
1	16.39	0.90	31.655	14.112	Perchlorate

This report has been created by IC Net

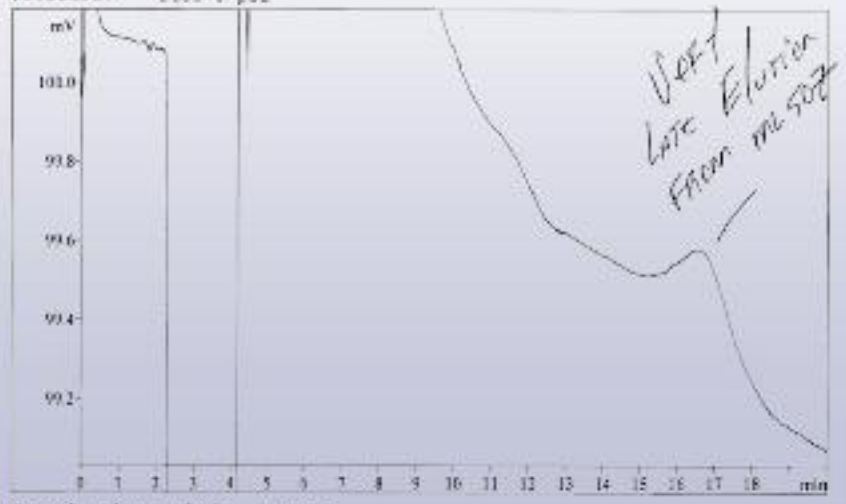
SAMPLE:

Vial number: 26
Volume: 1.0 µl
Dilution: 1.00
Amount: 1.0000

COLUMN: DX-AS16
Size: 4.0 x 250 mm
Number: 02362
Part size: 5.0 µm

ELUENT: 35 NaOH

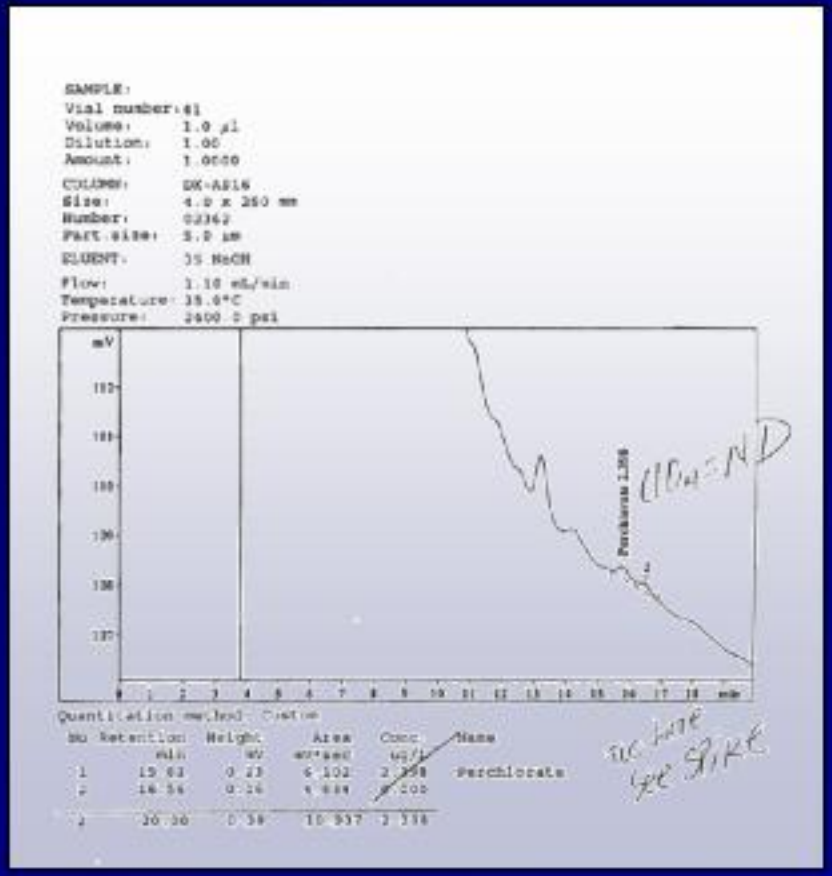
Flow: 1.10 mL/min
Temperature: 35.0°C
Pressure: 2600.0 psi

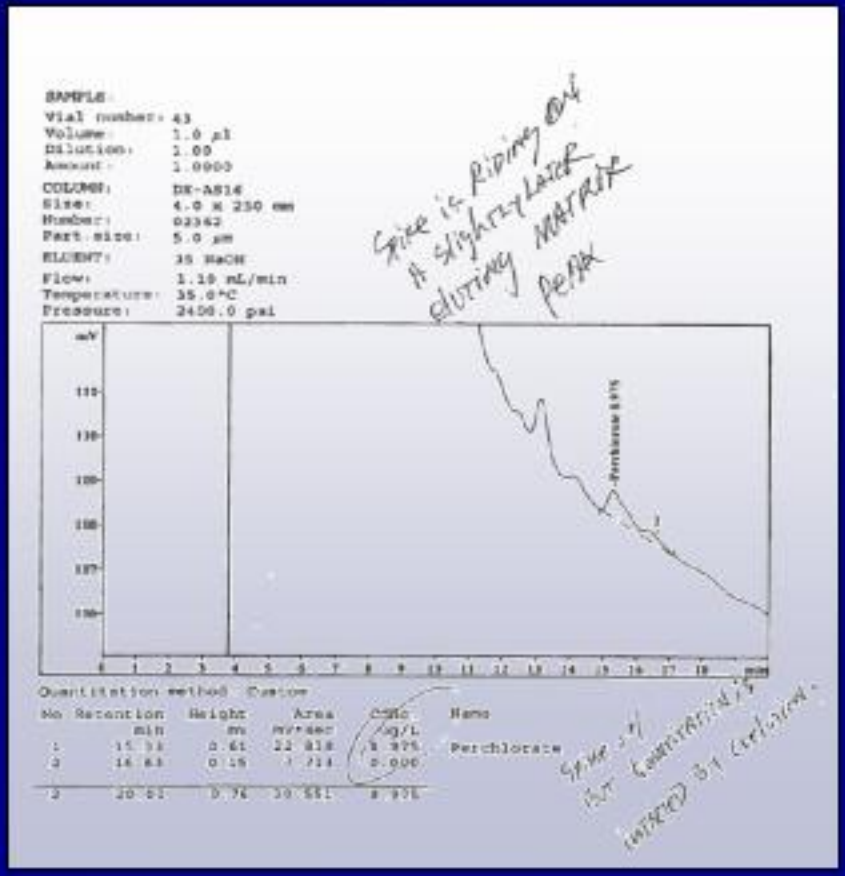


Quantitation method: Custom

No peaks
This report has been created by IC Net

Inconclusive Matrix Spike





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Liquid Chromatography with Dual Mass Spectrometry

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LC/MS/MS

- Leading edge technology
- DoD recommended
- Pending regulatory approval

Identification by LC/MS/MS

- LC separates perchlorate from other components in the same manner IC does
- Two mass spectrometers are used as detectors in place of the conductivity detector
- Unlike conductivity detectors, MS is a specific detector
  - Monitors molecular weights of parent (101/99 amu) and daughter ions (85/83 amu)

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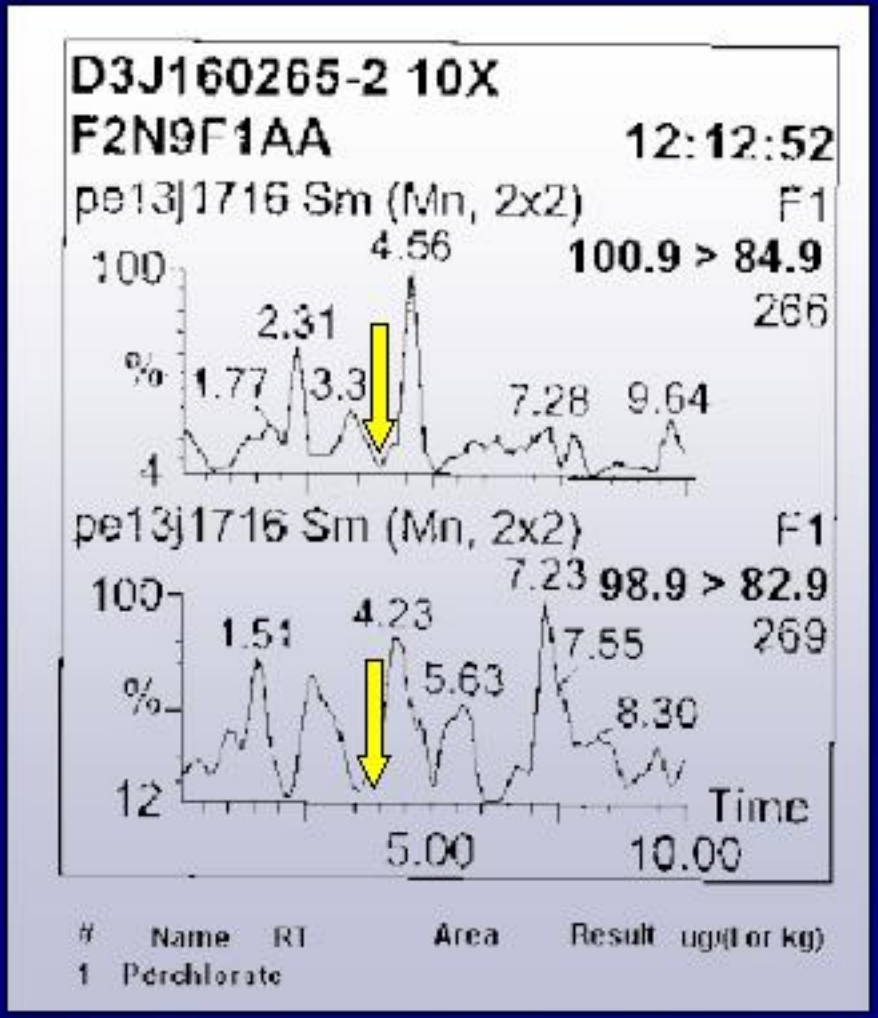
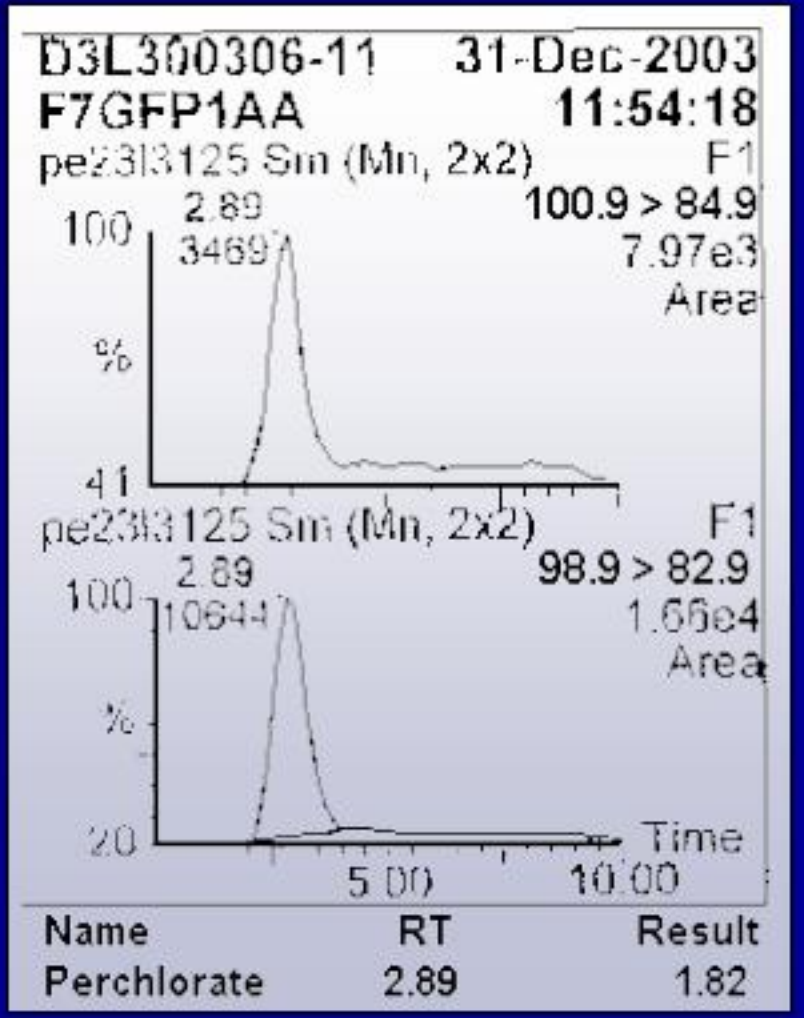
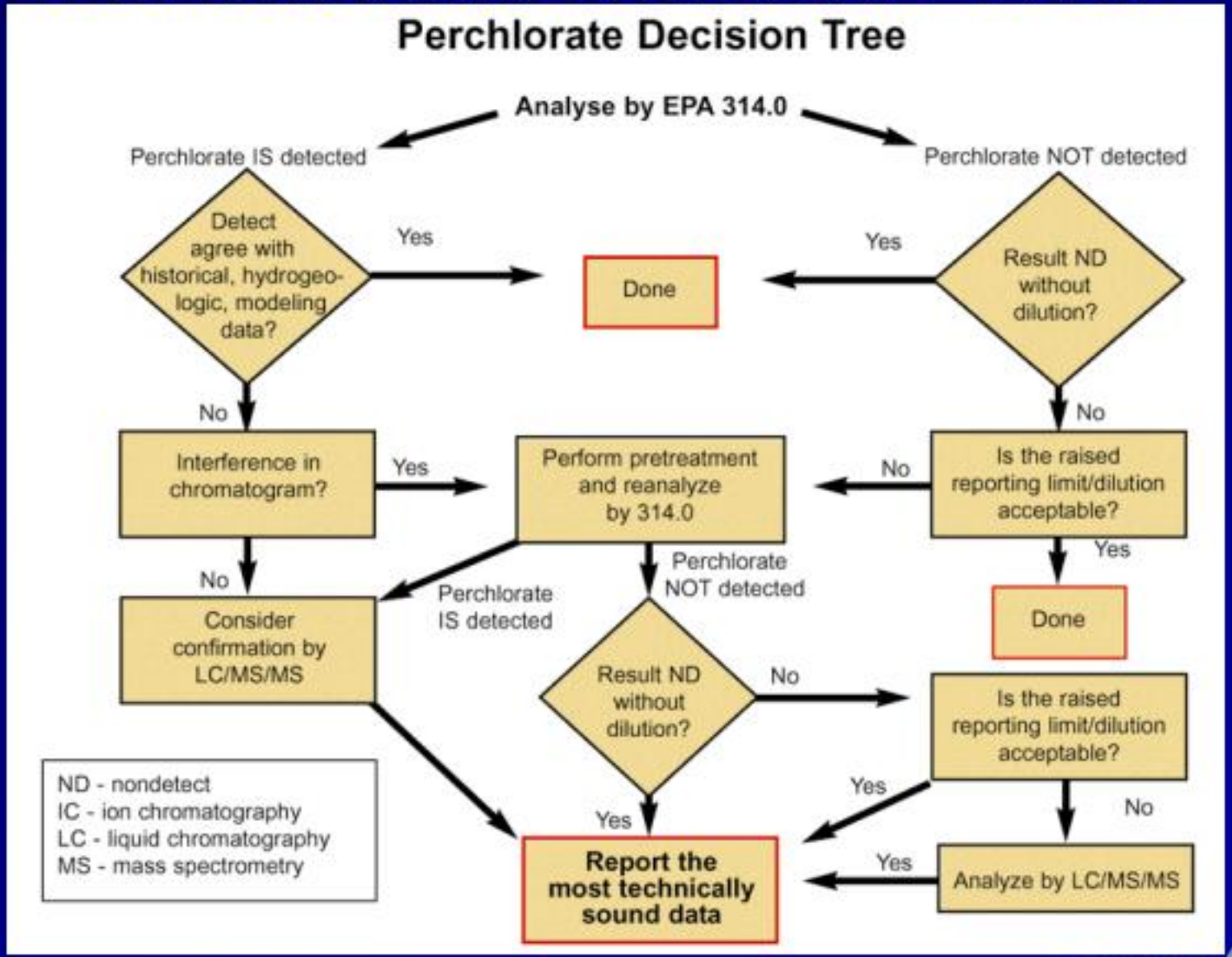
Results by LC/MS/MS





Perchlorate Decision Tree



Success Using the Perchlorate Decision Tree

- Approximately 1000 samples were collected and analyzed for perchlorate from August 2003 through January 2004
- 89 samples (about 9% of total) were pretreated and reanalyzed
- 39 samples (about 3% of total) were reanalyzed by LC/MS/MS - 24 detects and 15 non detects
- 10 perchlorate detects (about 0.4% of total) were confirmed by LC/MS/MS

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Success Using the Perchlorate Decision Tree

- Detects
  - 16 showed definite signs of interference
  - 2 had some interference
  - 6 had little or no interference
  - LC/MS/MS results equivalent to 314.0 for 9 confirmed results
  - 314.0 had over-reported 1 confirmed result (46 vs. 15 ppb)
- Non detects
  - 6 reported at raised reporting limits
  - 3 were highly suspicious
  - 6 were chosen randomly
- 58% false negative rate and 0% false positive rate

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Success Using the Perchlorate Decision Tree

- Saved $51,000 in analytical costs by not using LC/MS/MS exclusively
- Saved millions in remedial costs by not using 314.0 exclusively

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Summary

- Why use 314.0?
  - Cost
  - Capacity
  - Availability
  - Promulgated Method
- When to use LC/MS/MS?
  - Definitive Data
  - Critical Samples
  - Small Projects

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Thank You

Questions and Comments

Contact

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